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EUROPEAN PATENT APPLICATION

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54 **Devices and systems based novel superconducting material.**

57 A class of superconductive materials containing copper-oxygen bonding and with mixed cation-occupancy designed with a view to size and valence consideration yield useful values of critical temperature and other properties. Uses entail all applications which involves superconducting materials such as magnets and transmission lines which require continuous superconductivity paths as well as detectors (e.g., which may rely on tunneling).

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D scription

DEVICES AND SYSTEMS BASED NOVEL SUPERCONDUCTING MATERIAL

Background of th Inv ntion

5 This invention relates to superconductive material and apparatus and systems utilizing such material. Characteristics of preferred compositions herein give rise to apparatus designed advantages. Such characteristics include useful values of critical temperature and critical magnetic field. Certain of the compositions are free of characteristics which have been associated with radiation damage in prior materials.

10 The field of superconductivity has had a varied history from its beginnings -- from the discovery of the phenomenon by Kamerlingh Onnes in 1911. Implications of extreme practical significance were apparent from the start. Workers became enchanted with the thought of lossless transmission as well as implications on magnetic and other apparatus. The concept that has received so much attention in recent years -- that of "permanent" magnets of extremely high field values useful e.g. for containment of fusion reactions -- was not overlooked.

15 Advances in obtaining material with improved properties have been discontinuous. Experiments following the first discovery, while certainly substantiating the concept, established need for extremely low temperatures, i.e., low values of transition temperatures, T_c . Mercury (T_c 4 K) was discovered first, and lead (T_c 7 K) was discovered to be superconducting shortly thereafter.

20 There was little achievement either experimentally or in theoretical terms following the initial period until the 1940's when work on NbN yielded a T_c value of about 16K. Evolution and description of the concept was not broadly and effectively disseminated because of its German origin and circumstances surrounding World War II. A significant period of inquiry began subsequent to World War II. From the mechanistic standpoint, the most significant advance entailed identification of Type II superconductivity (Ginzburg and Landau, 20 Zh. Eksperim. i Teor. Fiz., pg. 1064 (1950)).

25 From a mechanistic-theoretical standpoint 1957 marks a most significant advance in understanding of superconductivity. The Bardeen Cooper Schrieffer Theory (for which a Nobel prize was subsequently awarded), (108 *Phys. Rev.*, pg. 1175 (1957)) gave rise to the understanding which has been implicit in all studies to the present time. Intensive worldwide effort was established by the activity of B. T. Matthias of Bell Laboratories and J. K. Hulm of Westinghouse resulting in the most significant A15 compounds exemplified by
30 Nb₃Sn. This was followed by identification of the members as well as of related alloy compositions generally containing Nb. This work gave renewed hope of practical applications working with a refrigerant more effective than liquid helium. Materials developed during this period continue to be studied extensively, and indeed serve very significant technological functions, e.g., in particle accelerators.

35 Efforts to develop materials with significantly higher values of T_c than that of Nb₃Sn (T_c = 18 K) were disappointing. Probably the culmination was the T_c value of 23.3K for Nb₃Ge in 1973 by L. Testardi at Bell Laboratories and J. R. Gavaler at Westinghouse.

The subsequent decade resulted in little advance in terms of T_c . Extensive study of a new category of material was, however, very important and plays a vital role in development of this invention. This study entailed compositions of barium bismuth lead oxide (BaPb_{1-x}Bi_xO₃). B. Batlogg, *Physica* 126B, 275 (1984). Most
40 significant, compositions in this category while attaining T_c values of only up to 13K depended upon metal-oxygen bonding for superconductivity.

Most recent origins of the present invention are traceable to the extremely significant work reported by IBM Zurich -- J. G. Bednorz and K. A. Muller (64 Z. Phys. B. - Condensed Matter, pp. 189 (1986)). Report of onset
45 T_c values in the 30K range in the La-Ba-Cu-O system stimulated intensive activity by a number of groups worldwide.

Significant consequences of work stimulated by the above are reflected in recent articles.

Workers at the University of Tokyo in Japan *J. Appl. Phys.*, significantly advanced understanding of the IBM work by identification of the superconducting phase as being of the K₂NiF₄ structure. The composition on which measurements were made in accordance with this publication was that of the IBM Zurich report.

50 C. W. Chu and co-workers at the University of Houston reported on the beneficial effect of application of hydrostatic pressure during measurement in *Phys. Rev. Lett.*, 58, 405 (1987). In a revision to this article made subsequent to the original submission date, comment was made on the substitution of strontium for barium.

The same issue of *Phys. Rev. Lett.*, 58 at page 408, reported true bulk conductivity at 39.2 K in the composition La_{1.85}Sr_{0.15}CuO₄.

55 The published works were accompanied and followed by a series of tantalizing rumors reporting "onset" temperatures well above the 77 K boiling point of liquid nitrogen. The March 2 issue of *Phys. Rev. Lett.*, (Vol. 58, 1987), contains two extremely significant papers representing advances prompted by the new findings. At page 908 et seq., workers at the Universities of Alabama and Houston report on compositions in the Y-Ba-Cu-O system evidencing T_c values well above 77 K. Their exemplary composition (Y_{0.8}Ba_{0.4})₂CuO₄ is described as multiple phase ("instead of the pure K₂NiF₄ phase" [associated with previously reported compositions]). Reporting a deviation in resistivity from the usual temperature relationship which is initiated at 93 K, the paper goes on to report attainment of zero resistivity at 80 K. Rather than associated attainment of
60 this value with the particular crystallographic phase, authors state "...high temperature superconductivity may

be associated with interfacial manifestations". At page 911 in the same issue of *Phys. Rev. Lett.*, the same authors in a separate article reached the specific conclusion "It is therefore evident that...above 77 K [T_c] may not be identified with...perovskite or...tetragonal layered structures..." Developments to date have taken on the drama of an international race with runners representing essentially every organization in any way affiliated with superconductivity. Events to date are reflected in an article on page 12 of the *Star-Ledger* for Tuesday, March 3, 1987. In this article, world-famous physicist John Rowell, Assistant Vice President of Bell Communications Research, reports as their "international contribution" the "...producing results identical to those achieved in general by scientists at the University of Houston...". Dr. Rowell explicitly confirms the multiphase nature of the superconducting material and, in fact, reports that "Only about 2%...is superconducting..."

Summary of the Invention

An important aspect of the invention takes the form of identification and isolation of the single crystallographic phase responsible for the superconducting characteristics that have been the subject of the world-wide quest. In a general sense, identification is of a perovskite or near-perovskite (referred to collectively as "perovskite") phase of specific composition. All included materials of the "perovskite" class are primarily pure quaternary or partially substituted quaternary copper oxides. Nominal compositions -- all single phase "perovskite" -- may be represented by the general formula $M_{3-m}M'_mCu_3O_{4-\delta}$, although specific materials of the general compositions of the reported multiphase material (*Phys. Rev. Lett.*, Vol. 58, page 908 et seq., March 2, 1987), are of the more somewhat specific nominal composition $M_2M_1Cu_3O_{9-\delta}$. The latter materials are based on a nominal 2:1 atomic ratio of divalent:trivalent cation inclusion in the M site. From the compositional standpoint, consistent with prior reported work, a class of materials of the invention are those in which M is predominantly barium and M' is predominantly yttrium. A more general class of materials of the invention are those of the first formula above in which M occupancy while averaging divalency, may contain an additional divalent ion such as strontium or calcium or in which the average valent state may be the consequence of occupancy by ions of differing valence values. Specific compositions described herein lack use of 1:1 occupancy by trivalent and monovalent (rare earth and alkali metal) ions. A class of materials of the invention depend upon predominant occupancy of M' by yttrium, although improved T_c values have been obtained by total substitution of europium. Other permitted M' ions are lutetium, lanthanum and scandium. With the exception of strontium and scandium and, of course, where valence averaging is intended, superconducting compositions of the invention have been based on total as well as partial M and/or M' occupancy.

Most useful superconducting properties have, in many instances, been traced to average copper valence ($Cu^{n+} = 2.0 < n < 2.67$). Oxygen content has been found to lie between the limits of 6.5 and 7.5 ($1.5 < \delta < 2.5$) for analyzed compositions herein.

Inventive implications apply to essentially all superconducting apparatus. The inventive findings in terms of preferred compositions have already provoked restudy of long-distance power transmission now made possible at liquid nitrogen temperatures. Other implications, of course, arise from the higher values of critical field with implications to fusion reaction containment, for example. Such purposes are consistent with materials characterized by continuous superconducting paths. Other purposed also well-known to prior workers include use in devices such as detectors and those dependent on tunneling phenomena such as Josephson junction devices as well as other devices which depend on weakly coupled superconductors and/or the large value of the superconducting gap. Application of particular value has been recognized in the literature *IBM Journal of Research and Development*, Vol. 24, No. 2, March 1980). The desire to decrease computing time which has provoked study of optical computers may take an alternate form in which interconnections, e.g., in a semiconductor computer, may be superconducting. Absence of resistance in a superconductor permits sealing down to result in a feasibly sized transmission line interconnect. In fact, use of compositions herein with T_c values sufficiently high to permit liquid nitrogen refrigerant is compatible with already-suggested increasing semiconductor mobility by liquid nitrogen cooling.

Brief Description of the Drawing

FIG. 1 is a diagrammatic representation of the ideal cubic perovskite structure. As described further on, it serves as a basis for structures in this invention which may entail distortions to lower symmetry and/or deviations from nominal stoichiometry.

FIGS. 2 and 3, on coordinates of resistivity and temperature, plot characteristics of materials made in accordance with the Examples on different coordinate scales. The curve form is useful in identification of the various values of T_c as the term is used in the art.

FIG. 4, on coordinates of magnetization and temperature, shows development of (superconductive) diamagnetic response, again, as plotted for typical materials produced in accordance with the Examples.

FIG. 5 depicts a cable design incorporating a superconducting element of an inventive composition.

FIG. 6 depicts a superconducting solenoid.

FIG. 7 represents a superconducting torus suitable for use for fusion reaction confinement.

FIG. 8 shows a Josephson junction device illustrative of devices dependent upon superconducting tunneling. FIG. 9 shows the current-voltage characteristics of the device of FIG. 8.

FIG. 9, on the coordinates of resistance and temperature, depicts a characteristic curve of the nature of FIGS. 2 and 3, but is included herein as illustrating an inventive composition with a deviation from the

normal conductor resistance/temperature relationship to yield what may be regarded as an unusually high superconducting onset temperature.

FIG. 10 depicts a semiconducting strip line suitable for use as interconnection linkage, e.g., in a semiconductor computer.

D tailed D scription

Most significantly, the origin of the invention is in terms of identification of essentially single phase material. Identification and the ability to reliably produce the single phase material here identified as "perovskite", naturally lead to total as well as partial substitutions, to establishment of criteria determinative of parameters such as cation concentrations, permit oxygen content (always deficient in terms of the prototypical composition) as well as average valence state of the copper ion (crucial in terms of the mechanism which may be regarded as responsible for supplying conductive electrons). From a practical standpoint, the "perovskite" structure relative to earlier structures permits expeditious sintering, generally at lower temperature. The role of the perovskite is crucial so long as the superconducting element is not a single crystal (e.g., in the ceramic form of many of the reported experiments herein). An important attribute has to do with facilitation of larger crystallites and as possibly aided by improved intergrain contact with resulting enhanced current-carrying capability.

Isolation of small single crystals has permitted reliable identification of the repeated cell units. In addition, thermogravimetric analysis has been employed to yield the oxygen-deficiency values reported in this description. Critical currents so far measured have been limited not by the superconductor, but by the measuring apparatus -- critical current values are in excess of 1,000 amperes per square centimeter (of superconductor cross-section). These measurements have been limited by melting of (normal conductive) contacts and consequent heating and impairment of underlying superconductor. Critical fields are high -- values of 40-50 Tesla at 77 K have been seen (1 Telsa = 10 Kgauss).

Substitutions -- of course with the requirement that the superconducting "perovskite" be retained -- have resulted in significant increase in relevant T_c values $T_{c\text{onset}}$ as well as $T_c R - 0$. Perhaps of equal importance, substitutions of elements as common as lanthanum, calcium and sodium result in material cost saving.

Two factors played significant roles in identification and in the ability to reliably produce single phase material of the ascribed superconducting characteristics. It is appropriate to describe the inventive advance in terms of two aspects: (1) structure of the phase, and (2) composition (identification of which was essential to isolation of (1)).

Structure

Materials of the invention are essentially single phase. By this it is meant that the materials herein are single phase preferably to at least 95 mole percent as determined by powder x-ray diffraction. The particular value, 95 percent, is chosen as corresponding with the expected measurement precision of ordinary apparatus - procedures. While such "truly" single phase material is to be preferred and will doubtless be the ambition for practical usage, compositional as well as preparatory considerations (e.g., film formation) leads to the more general requirement that materials be single phase to 75 mole percent. Even somewhat larger amounts of second phase material are permissible for uses in which maximum current density is not required.

It is most significant that the single phase so identified is "perovskite". The quoted term as used herein is meant to include not only prototype, truly cubic material, but very significantly distortions therefrom. As indicated, other variation from the nominal perovskite is in terms of stoichiometry. Analyzed materials of the invention show oxygen occupancy of 6.5-7.1 significantly below the nominal composition of 9 for a non-deficient perovskite. This translates into the δ values of 1.9 to 2.5 in terms of the formula containing $O_{9-\delta}$. A somewhat wider range is still expected to superconduct. A preferred category of materials herein show a specific form of distortion of such preferred materials (materials having the higher T_c values) while variables share in common a magnitude such that observation of the distortion is observed on ordinary instrumentation as used in x-ray powder diffraction.

There are two significant compositional contributions to the structure. These are discussed in more detail in a following section relating (a) to observed oxygen deficiencies which reduces the coordination number of a portion of the copper from six to five or possibly four, and (b) mixed occupancy of the "A site" (in the prototypical representation ABO_3), i.e., occupancy by ions represented as M and M' in the general formula above -- gives rise to a further variation. X-ray diffraction studies, in indicating single phase material, translate into substantial ordering of M and M' ions in selected compositions which, in turn, gives rise to a unit cell size larger than that of the primitive cell corresponding with the single formula unit ABO_3 . X-ray diffraction measurements of a preferred composition -- nominal $Ba_2YCu_3O_{6.9}$ indicate a crystallographic unit cell of orthorhombic symmetry of size $a=3.87$, $b=3.86$, $c=11.67$ Angstroms. This crystallographic cell is a "supercell" of the cubic ABO_3 and is of three times the volume due to subtle ordering effects. Other compositions may show different "supercells" or exhibit "supercells" whose diffraction signatures are too weak to be observed by conventional x-ray powder diffraction techniques. Such supercells are well known in perovskite structure type materials. Isolation of single crystalline materials has permitted verification of the above. In compositions herein in which M and M' ions differ in size sufficiently (e.g., in terms of an ionic radius ratio of at least 1.2), these materials are truly ordered for compositions in which inclusion of M/M' ions nominally follows the ratio 2/1, the repeating unit includes three primitive cells. While preferred compositions

generally meet the ion size requirements for ordering, other superconducting compositions of the invention do not. So, for example, compositions of Examples 6 to 11 are based on M/M' radii which do not inherently result in ordering. Considerations such as material cost and ease of processing may lead to selection of such compositions which, in these terms, may be "disordered".

It is essential to the invention that materials meet all structural criteria as set forth in this section. Those familiar with the development of superconductivity will recognize the significance of the identification of the highly symmetrical perovskite structure. The relationship has most importantly been observed experimentally and more recently has been explained in theoretical terms, for example, in terms of band theory. The relationship plays a role in the Bardeen Cooper Schrieffer (BCS) theory of superconductivity.

Composition

It is noteworthy that A site occupancy (relative numbers of M and M' ions) represents a large departure from the compositions (of the mixed phase materials) which have received so much attention. In fact, the nominal ratio of 2:1 for M:M' ions is nearly the inverse of the ratio in the materials reported thus far (of the mixed phase) materials which provoked world-wide inquiry. In terms of critical temperature, T_c , preferred compositions are those in which M is primarily barium as described. Partial substitution of barium by other ions, e.g., calcium and strontium, may be dictated by economic or processing considerations. Reports of the mixed phase materials were based on use of yttrium. Compositions of the invention may also utilize yttrium although total or partial substitution of other elements has been useful (see Examples herein). Europium, in particular, yields increased values of T_c . Total substitution by lutetium as well as lanthanum has also been employed as has (substantial) partial substitution by scandium. As is seen from the Examples, partial substitutions, e.g., at the 25 mole percent level, do not substantially affect T_c in many instances. The significance of processing temperature is seen repeatedly. Total occupancy of M' by lanthanum in Example 6 produced a material with a $T_{cR=0}$ value of only 25 K while the same nominal composition in Example 11 yielded a value of 80 K. The difference is ascribed to the anneal temperature. In Example 6, annealing in oxygen at 1 atmosphere was a temperature of 950°. In Example 11, the anneal conditions were unchanged but for a change in the anneal temperature of 700° C from 900° C.

The 2:1 A site occupancy is considered essential to form superconducting perovskite structures with small rare earths (Y, Eu, Lu). Experiments thus far with compositions deviating by as little as 10 percent, result in multiphase material. For larger rare earths, e.g., La, considerable variations in the M/M' ratio is tolerated structurally, although larger variation generally does not lead to optimized superconductive characteristics.

The present invention is importantly premised on identification of a reproducible preparation of single phase material. It has been indicated that the 2:1 A site occupancy may give rise to a unit cell containing more than a single ABO_3 unit. Partial substitutions, e.g., at the 25 mole percent level as reported in the Examples, give no x-ray indication of deviation -- such materials continue to be identified as single phase. It is observed, however, that partial substitution, like total substitution, gives rise to some change in the degree and type of distortion from cubic perovskite. Again, it has generally been observed that reduction in distortion corresponds with some lessening in T_c .

Consistent with reported results pertaining to the mixture phase materials, it is concluded that barium and yttrium are ideal M, M' occupants. Substitution, whether partial or total, is preferably by ions that approach the size of the ions that are replaced. Some materials of the Examples are consistent in depending upon partial substitution of yttrium by the smaller trivalent ion, scandium, or the larger trivalent ion, lanthanum, although others show larger tolerance for size change. Substitution of the divalent ion in the M site also meets such size criteria. One such material described in Example 4 entails 25 mole percent substitution of the divalent alkaline earth ion barium by the next smaller alkaline earth ion of strontium.

Oxygen Deficiency

It is well known that copper-based perovskites can be -- generally are -- oxygen deficient. Material of the invention which have been examined are no exception. Measurements made in the usual manner (thermogravimetric analysis using hydrogen reduction at 950 ° C) yield values of δ (in the formula $M_2M'Cu_3O_{9-\delta}$) within the range of from 1.5 to 2.5. Conductivity is largely dependent upon electrons yielded by the coexistence of both divalent and trivalent copper. The observed oxygen stoichiometry yields an average copper valence centering about 2.3. As discussed under "Material Preparation", average valence state is dependent upon processing conditions. Specifically varying the temperature and time of oxygen anneal varies this quantity.

Material Preparation

Material specification in accordance with the invention depends upon the nature of the intended use. For power transmission, or any other current-carrying application, it is required that there be a continuous superconducting path. For detector and other device use (e.g., Josephson junction devices) in which tunneling might be permitted or even required, it is necessary only that there be sufficient superconducting phase to satisfy such use.

For many purposes, it is an advantage of the invention that fabrication of superconducting elements may utilize standard ceramic processing.

Appropriate starting materials are mixtures of metallic oxides, hydroxides, carbonates, hydrates, oxalates or

other reactive precursors in the appropriate ratio to obtain the desired final composition. Starting material may be produced by wet or dry mixing, by co-precipitation of materials from solution, or by any other method which results in intimate mixture of reactive particles.

Mixtures of starting materials can be fired in air, oxygen or other non-reducing ambient at temperatures sufficient to facilitate chemical reaction between constituents and to begin formation of the desired phase. Firing temperatures as noted are composition-dependent so that choice of temperature may radically affect T_c for certain compositions. Typically, temperatures are between approximately 700 and 950 C for times of between a few hours and several days until the desired phase is either fully or partially produced. The "calcined" material is then formed into the ceramic body of desired shape by standard ceramic processing techniques such as hot or cold pressing, extrusion, slipcasting, or other such techniques appropriate to the geometry of the desired (green body) object.

The material in final form is fired at a temperature sufficiently high to complete chemical reaction of components ("reactive sintering") if not accomplished in step (2) and for densification. This "sintering" is conducted so as to reduce voids to the point where the density of the ceramic body is sufficient to allow obtaining favorable electrical and mechanical properties. For most favorable results, the material is fired in an ambient environment with greater partial pressure of O_2 than that of air (.2 atm.). However, material fired in air may have acceptable superconducting properties. (Air is not the desired processing environment since the use of too high a temperature may result in undue oxygen loss and consequently degradation of properties.)

While the description above is important for many purposes, material preparation may take other forms. An alternative is preparation of thin films for Josephson junction and other devices. Workers in the field know of many film-forming procedures, e.g., magnetron sputtering, diode sputtering, reactive ion sputtering, ion-beam sputtering and other thin film deposition techniques including evaporation. "Conductor" structures may take on the form of continuous strands, however produced. Initial formation may utilize techniques as applied to other brittle glass-like material. In this approach, the structure reverts to one that is crystalline before attainment of superconductivity. One technique which has been applied to other brittle superconductors entails extrusion within a protective sheathing of copper or other ductile material.

Since the material is oxidic another approach may entail formation of an alloy of the designated metals followed by oxidation.

Generalized Preparatory Approach As Used in the Examples

Here the procedure followed in each of the numbered examples is set forth:

1) starting materials are powders of lanthanum hydroxide, strontium carbonate, calcium oxide, copper oxide, barium oxide, yttrium oxide, europium oxide, lutetium oxide, praseodymium oxide, and scandium oxide. While much of the work entailed relative high purity, many rare earths contain finite amounts of other rare earths which are difficult to remove. It is noteworthy that high purities are not required for preparation of suitable material.

2) starting materials are weighted in appropriate quantities to yield the desired composition. They are then further pulverized in a mortar and pestle.

3) materials from step 2 are then fired (for comparison purposes reported examples used a temperature of 950° C for a period of approximately 16 hours).

4) in some cases the materials were pulverized and then refired in air or oxygen for 16 hours.

5) Materials are pulverized and pressed dry into shape suitable for experimentation at a pressure of between 5,000 and 10,000 psi. (In the examples reported the shape was that of a disc of approximately 1 cm diameter and 1mm thick).

6) The discs are next fired at a temperature of 950° C for two hours in oxygen in Examples 1 through 7. As seen from other Examples, lower temperatures were sometimes preferable (Examples 9 through 15 were fired at 700° C).

7) Materials are allowed to cool to ambient room temperature in flowing oxygen gas.

As stated, the above conditions were for purpose of comparison. Other preliminary work has established the value of varying many of the conditions set forth. For example, the repeating of step 4 to assure a degree of uniformity can be omitted -- may even desirably be omitted. Clearly, the temperatures stated are non-critical, the requirement being only that the required composition-phase is produced in sufficient quantity as described. Consistent with the description above, other considerations may dictate deliberate abbreviation in processing to avoid production of pure single-phase material.

The technique used to identify the nature of the final material is set forth: a portion of the finally annealed disc is pulverized, and a powder X-ray diffraction pattern is made. The particular technique used was powder diffractometry, although other techniques such as Debye-Scherrer or Guinier photography may also be employed. (B. D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley Publ. Co., Inc., Reading, Mass. (1978)).

The Examples

Examples are expressed in terms of the final nominal compositions and measured properties. These compositions and properties are summarized in the Table.

TABLE

COMPOSITIONS AND SUPERCONDUCTING TRANSITION TEMPERATURES FOR EXAMPLE MATERIALS

Example	Composition	T _c ^{onset}	T _c ^{midpoint}	T _c ^{R=0}	T _c ^M	Anneal T in O ₂
1.	Ba ₂ YCu ₃ O _{9-δ}	93.5	93.0	91.5	90.0	950
2.	Ba ₂ YCu ₃ O _{9-δ}	88	72	55		950 (air)
3.	Ba ₂ YCu ₃ O _{9-δ}	88	81	72		950 (3 atm O ₂)
4.	Ba _{1.5} Sr _{0.5} YCu ₃ O _{9-δ}	80	87	86		950
5.	Ba ₂ Y _{0.75} Sc _{0.25} Cu ₃ O _{9-δ}	93	92	87		950
6.	Ba ₂ LaCu ₃ O _{9-δ}	49	34	25		950
7.	Ba ₂ Y _{0.75} La _{0.25} Cu ₃ O _{9-δ}	92	87	82		950
8.	Ba ₂ YCu ₃ O _{9-δ}	182	88	84		600 (quench)
9.	Ba ₂ EuCu ₃ O _{9-δ}	96	91.5	93.5		700
10.	Ba ₂ Eu _{0.9} Y _{0.1} Cu ₃ O _{9-δ}	96	95.3	94.7		700
11.	Ba ₂ LaCu ₃ O _{9-δ}	77	60	48		700

TABLE (CONT'D)

COMPOSITIONS AND SUPERCONDUCTING TRANSITION TEMPERATURES FOR EXAMPLE MATERIALS

Example	Composition	$T_{c\text{onset}}$	$T_{c\text{midpoint}}$	T_{c0}	T_c^M	Anneal T in O_2
12.	$BaCaLaCu_3O_{9-\delta}$	82	81	80		700
13.	$Ba_2Eu_{0.75}Sc_{0.25}Cu_3O_{9-\delta}$	95	92	90		700
14.	$Ba_2Eu_{0.9}Pr_{0.1}Cu_3O_{9-\delta}$	85	82	80		700
15.	$BaCaYCu_3O_{9-\delta}$	83	80	77		700

The characteristic terms in which the Examples are defined are set forth below. Examples 1, 2 and 3 differ one from the other solely in terms of the atmosphere used during anneal. In Example 1, the atmosphere was

oxygen at 1 atmosphere of pressure, in Example 2, it was air also at 1 atmosphere, in Example 3, the anneal atmosphere was oxygen at 3 atmospheres of pressure. Example 8 was air quenched from a 600° C oxygen anneal.

Properties

Description of transition temperatures, T_c , in the literature has not been free of ambiguity. Frequently measured results are in terms of: (1) ($T_{c\text{onset}}$) what is usually called "onset temperature" which is in itself ambiguous. The term is intended to signify the first anomaly in a measured characteristic indicative of superconductivity (examples include variations in the slope of resistivity v. temperature, decrease of magnetic susceptibility, etc.), (2) ($T_{c\text{midpoint}}$) the resistive midpoint, i.e., the resistance value which is 1/2 that of the onset and absolute zero values, (3) ($T_{cR=0}$) more meaningful measure directly indicative of true superconductivity, i.e., resistive-less conduction of current (zero resistance), electrical resistance, and (4) (T_{cM}) the most stringent measure (as reported herein) involving the expulsion of magnetic flux. (By this technique the fraction of the volume which is superconducting may be determined.)

Materials produced in accordance with the examples were found to have the values of T_c given in the Table. (Many of the materials prepared in the examples were measured by more than one of the described techniques as indicated above).

In all instances reported in the examples, product was established as exhibiting a perovskite structure. Again, for comparative purposes, it was found useful to select examples in which the sample was substantially single-phase.

FIG. 1 presents the atomic arrangement of the unit cell of materials of the perovskite structure type. The structure has been described in detail in standard references. The symbols of the type marked by 71 are representative of the positions of the A site atoms in the prototype material; the corners of the octahedra as marked by 72 are representative of the oxygen atoms; and symbols of the type marked 73 are representative of the copper atoms. The unit cell represented in the Figure has cubic symmetry, that is, that the elementary repeat distances in the directions denoted by arrows marked 74, 75 and 76 are equal in length to each other. There are many distortions and type of nonstoichiometry in perovskites which are detailed in standard references. Most of the compositions herein are tetragonal, but Example 2 is cubic or nearly so.

FIG. 2 is illustrative of the resistive technique for measuring superconductivity. The resistivity measurement is made by a standard 4-point probe. The abscissa units are temperature in Kelvin, K. It is seen that curve 1 follows a constant slope upon decrease of temperature to about 110 K, below which the resistivity decreases more quickly, followed by a more abrupt break 2 indicative of onset of superconductivity. Point 3 is the "mid-point resistive" value, in this instance occurring at 93 K. Point 4 represents the temperature at which all resistance to the flow of electricity occurs and is 91.5 K in this sample.

FIG. 3 is a blowup of FIG. 2 showing the same features in more detail. FIG. 4, in units of magnetization on the ordinate in terms of 10^{-2} emu versus temperature in Kelvin on the abscissa, are illustrative of the results of magnetization measurements. The particular sample is that of Example 1. The procedure followed for this Example and for all others reported involved first cooling the sample to 4 K, a magnetic field was then applied and the temperature increased while measuring the magnetization used in a commercial SQUID magnetometer. For the particular sample plotted, the field applied was 18.5 Oe resulting in a magnetization of -3.10×10^{-2} emu at 10 K and sharply turned up to become positive above 90 K.

In FIG. 5, the structure shown is described in detail in G. Bogner, "Large Scale Applications of Superconductivity", in *Superconductor Application: SQUIDS and Machines*, B. B. Schwartz and S. Foner, eds. (Plenum Press, New York, 1977). Briefly, structure depicted consists of an outer sheathing 31, thermal insulation layers 32a and 32b, evacuated annular regions 33a and 33b, spacers 34, nitrogen-filled annular region 35, heat shield 36, and coolant regions 37a and 37b (it is a feature of the inventive structure that coolant may consist of liquid nitrogen in contradistinction with the liquid helium or hydrogen required of earlier structures). Element 38 is a superconductor material in accordance with the invention. FIG. 6 shows an annular cryostat 41 filled with liquid nitrogen and containing turns 42 of a material herein. Terminal leads 43 and 44 are shown emerging from the coil. Magnetic test structure of FIG. 7 is described in R. A. Hein and D. U. Gubser, "Applications in the United States", in *Superconductor Materials Science: Metallurgy, Fabrication, and Applications*, S. Foner and B. B. Schwartz, eds., (Plenum Press, New York, 1981). The superconducting element shown as windings 51 are made of a material herein. The structure is considered exemplary of those expected to find broad-scale use for containment of fusion reaction.

FIGS. 8 and 9 depict the IV characteristic (9) of the Josephson junction device shown schematically in 8. The structure consists of two superconducting layers 61 and 62 separated by a tunneling barrier 63. Use of material of the invention (not necessarily identical) for 61 and 64 permit usual Josephson action at higher temperatures than previously permitted. Josephson junction devices are described in M. R. Beasley and C. J. Kircher "Josephson Junction Electronics: Materials Issues and Fabrication Techniques", *ibid*.

FIG. 10 is a perspective view of a section of superconducting stripline. Structures of the type depicted usefully serve as interconnections (rather than many-kilometer long distance transmission). It is structures of this type that are expected to permit operation at significantly increased speed of present commercial apparatus. The structure which is depicted in *J. Appl. Phys.*, Vol. 49, No. 1, page 308, January 1978, consists of superconducting strip 80 insulated from superconducting groundplane 81 by dielectric layer 82. Considerations entailed in dimensioning the structure depend upon intended use and are generally described

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in the *J. Appl. Phys.* reference.

FIG. 11 is on coordinate units in milliohms on the ordinate and temperature in Kelvin on the abscissa shows resistive values measured in the manner described in the description of FIG. 2. The particular composition is that of Example 8 ($\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$). The significance of processing temperature on superconducting properties is exemplified by the characteristics shown in FIG. 11 with particular attention to evidence of $T_{\text{C onset}}$. Specifically, point 90 represents a break in the normal resistance the temperature characteristic (of usual conductors). The change in slope at the temperature of 182 K (point 90) represents a well-marked break in the usual resistance temperature dependence shown in conventional conductors. This behaviour is consistent with reported measurements by other workers identified as $T_{\text{C onset}}$. Point 91, representing the conventional $T_{\text{C midpoint}}$, is at a temperature of 88 K. Full superconductivity ($T_{\text{C R-0}}$) at the intercept with the abscissa is at about 85 K.

The FIG. is included as representative of the significance of processing conditions on superconducting properties. The particular composition is nominally identical to that of Example 1 which manifests only a more conventional onset temperature of about 93.5 K (in this instance, corresponding with $T_{\text{C midpoint}}$ and $T_{\text{C R-0}}$ values of 93.0 K and 91.5 K), the characteristic which was varied for the purpose of FIG. 11 was the anneal. While the sample of Example 1 was annealed in the range from 600-700° C in oxygen and was subsequently slow cooled (turning the annealed furnace off resulted in attainment of room temperature in a period of about 1 hour). The sample of FIG. 11, on the other hand, while annealed in the same temperature range under the same conditions, was repeatedly quenched to room temperature by plunging in water.

Claims

1. Superconducting element comprising a body CHARACTERISED BY at least one substantially single-phase composition nominally of the perovskite structure which is at least one of the nominally quaternary or substituted quaternary copper oxides of the nominal formula $\text{M}_2\text{M}'\text{Cu}_3\text{O}_{9-\delta}$ in which M ions are substantially divalent, M' ions are substantially trivalent, and δ is numerically at least 1, and in which divergence from the nominal formula amounts of M and M' is a maximum of 10 at percent.
2. Superconducting element of claim 1, CHARACTERISED IN THAT M contains Ba.
3. Superconducting element of claim 2, CHARACTERISED IN THAT M contains calcium.
4. Superconducting element of claim 3, CHARACTERISED IN THAT the number of ions of calcium is approximately equal to the number of ions of barium.
5. Superconducting element of claim 3, CHARACTERISED IN THAT M is predominantly Ba.
6. Superconducting element of claim 1, CHARACTERISED IN THAT M includes a minor amount of Sr.
7. Superconducting element of claim 3, CHARACTERISED IN THAT Sr is contained in maximum amount of 25 atom percent of M.
8. Superconducting element of claim 1 CHARACTERISED IN THAT M' is predominantly at least one element selected from the group comprising of Y, La, Eu and Lu.
9. Superconducting element of claim 8, CHARACTERISED IN THAT M is at least 75 atom percent of at least one element of the group comprising of Y, La, Eu and Lu.
10. Superconducting element of claim 9, CHARACTERISED IN THAT M' is predominantly Y.
11. Superconducting element of claim 9, CHARACTERISED IN THAT M' is predominantly Eu.
12. Superconducting element of claim 10, CHARACTERISED IN THAT M' includes Sc.
13. Superconducting element of claim 11, CHARACTERISED IN THAT M' includes Sc.
14. Superconducting element of claim 12, CHARACTERISED IN THAT M' is at least 75 atomic percent Y.
15. Superconducting element of claim 13, CHARACTERISED IN THAT M' is at least 75 atomic percent Eu.
16. Superconducting element of claim 1 CHARACTERISED IN THAT M consists substantially of Ba and M' consists substantially of Y.
17. Superconducting element of claim 1 CHARACTERISED IN THAT M' consists substantially of Eu.
18. Superconducting element of claim 1, CHARACTERISED IN THAT M consists substantially of Ba and M' consists substantially of Y.
19. Superconducting element of claim 1, CHARACTERISED IN THAT M consists substantially of Ba and M' consists substantially of Eu.
20. Apparatus which depends for its operation upon superconducting current which includes an element as described in any one of claims 1 through 19.
21. Magnetic apparatus which in operation produces a magnetic field by virtue of superconducting current which includes an element claimed in any one of claims 1 through 19.
22. Transmission line for carrying electrical power by means of passage of superconducting current in which the path for such current is defined by an element as claimed in any one of claims 1 through 19.
23. Transmission line of claim 22 comprising a superconducting strip and a superconducting groundplane electrically insulated from each other by a dielectric layer.
24. Transmission line of claim 23 in which the said superconducting strip and groundplane are substantially rectilinear in cross section.

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FIG.1

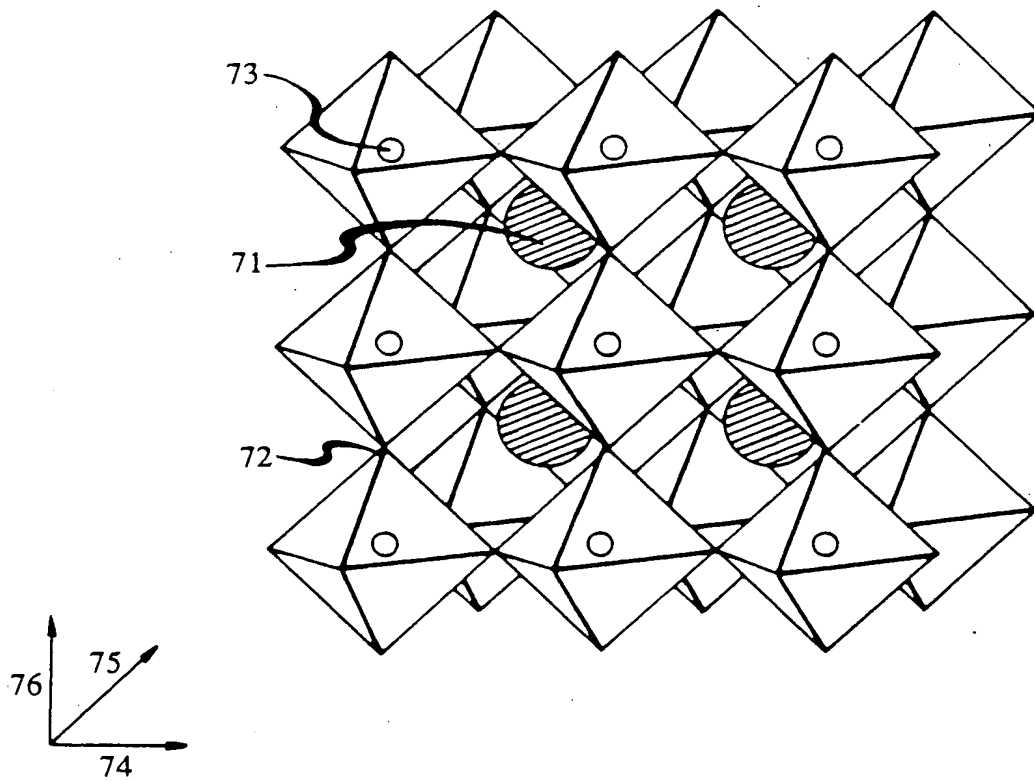


FIG. 8

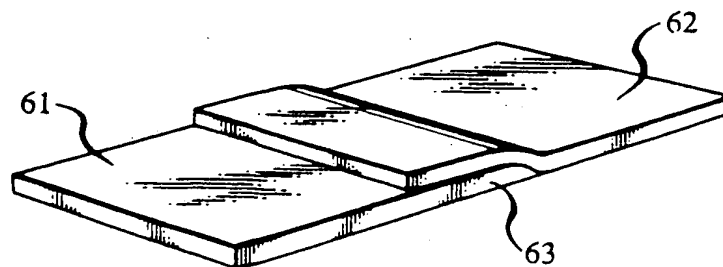


FIG. 2

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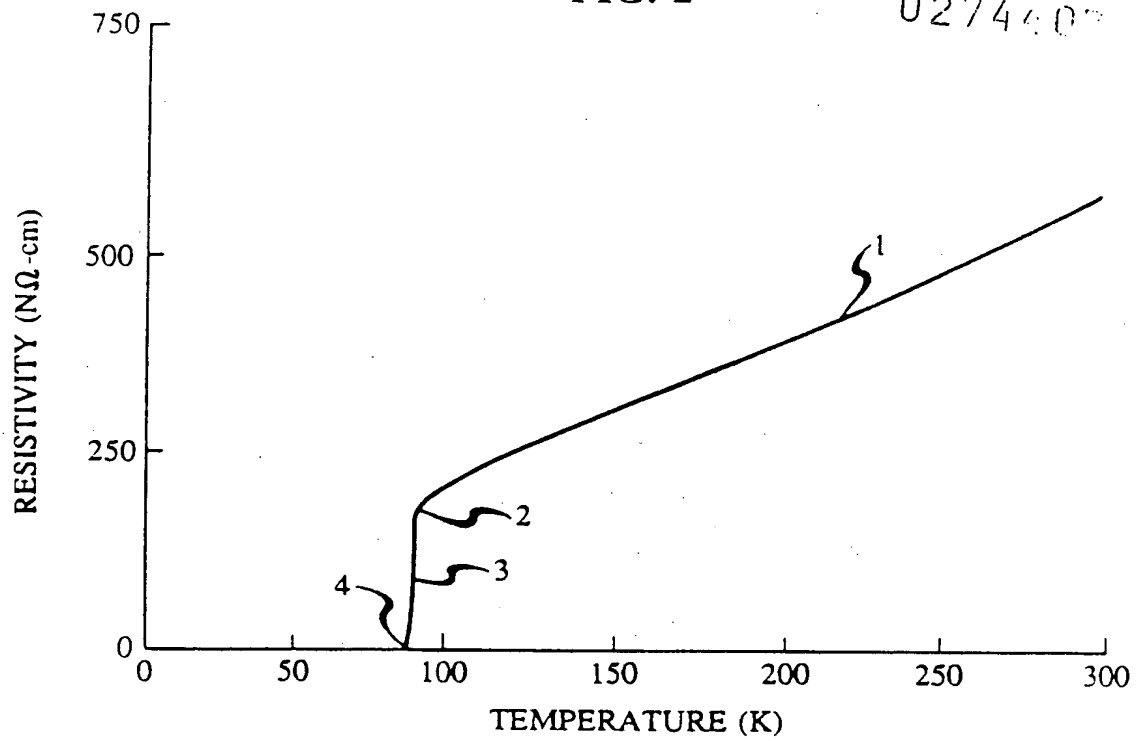
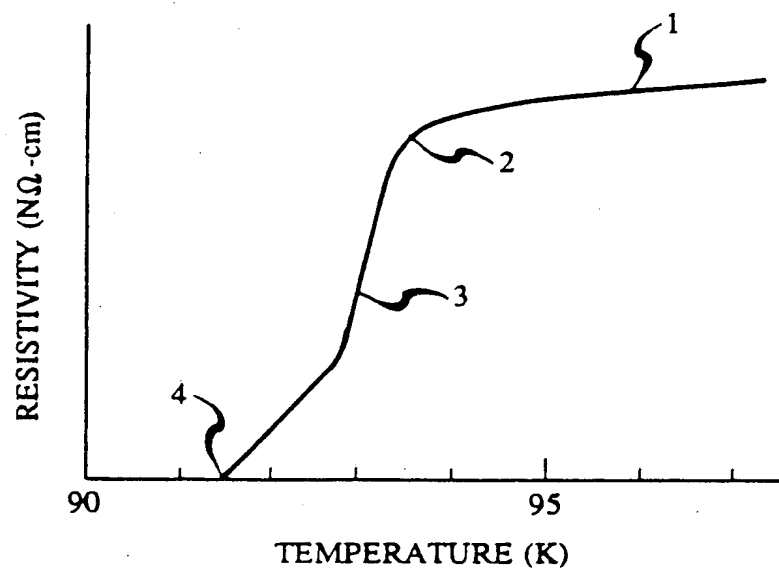
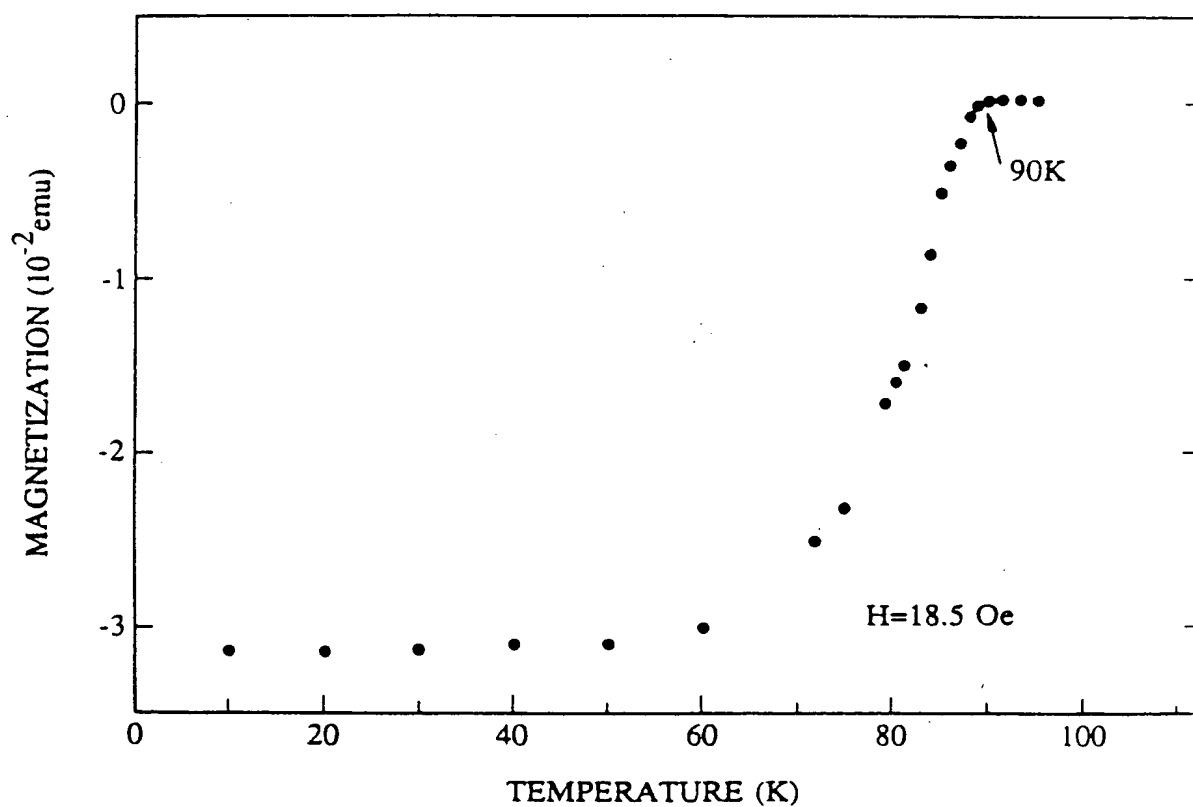


FIG. 3



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FIG. 4



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FIG. 5

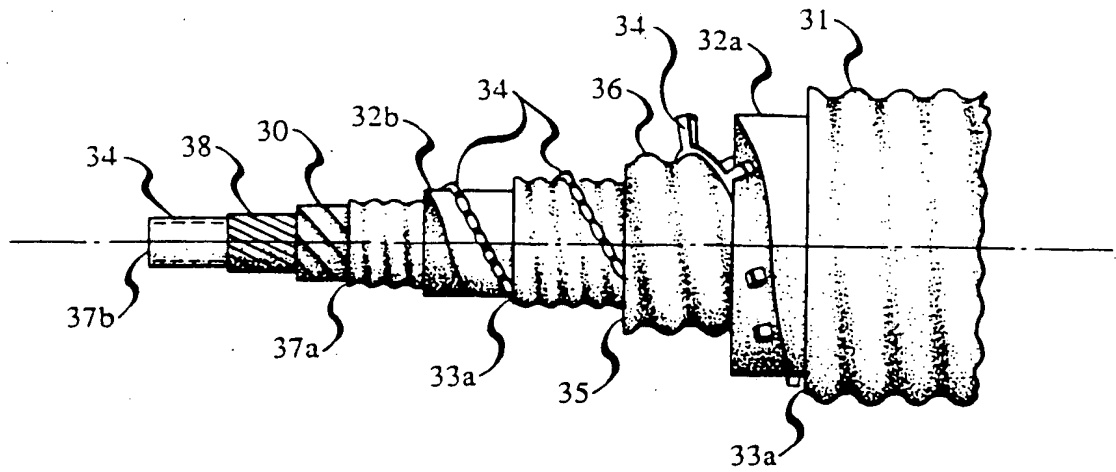
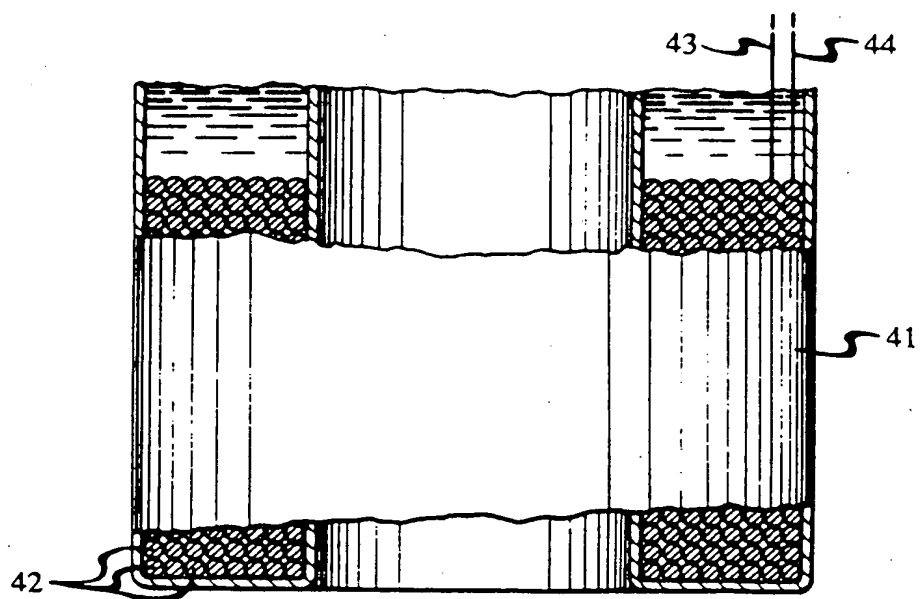


FIG. 6



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FIG. 7

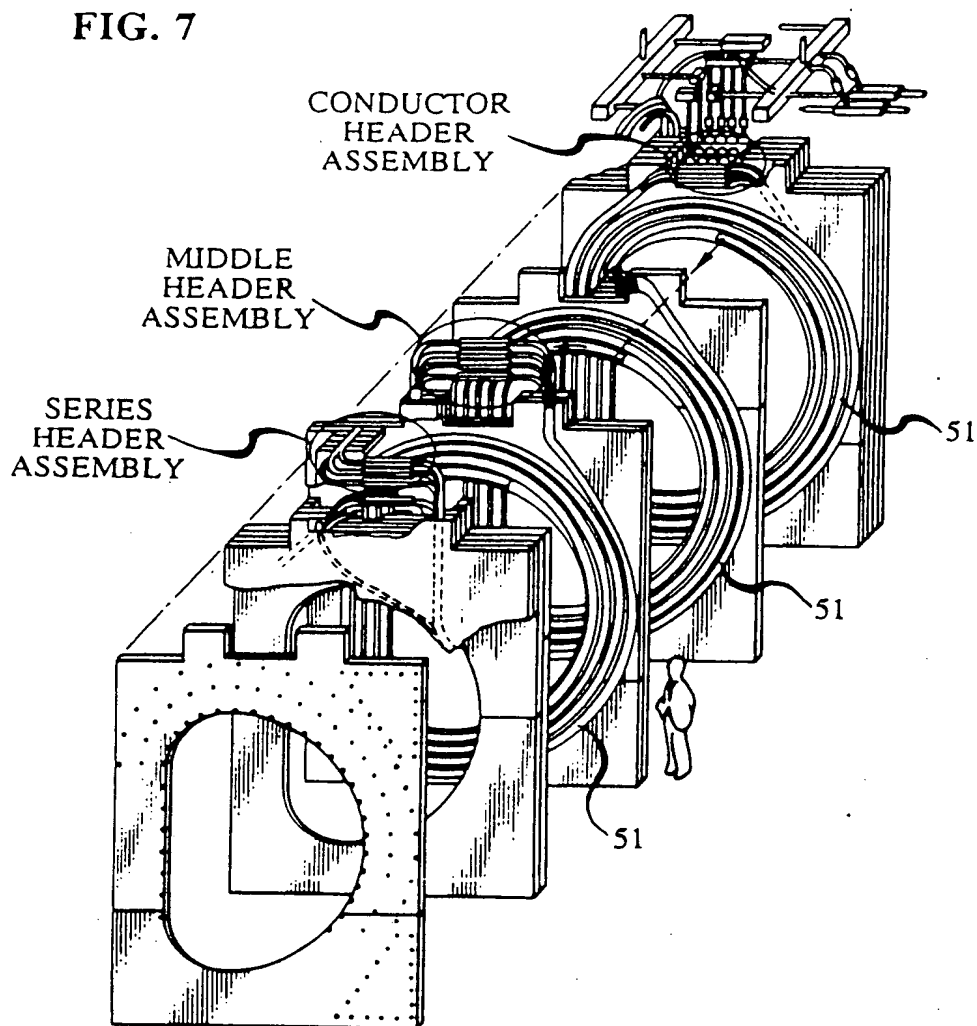
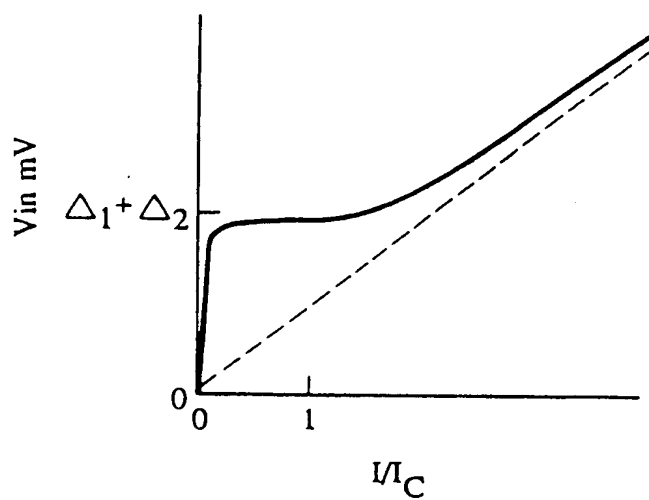


FIG. 9



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FIG. 10

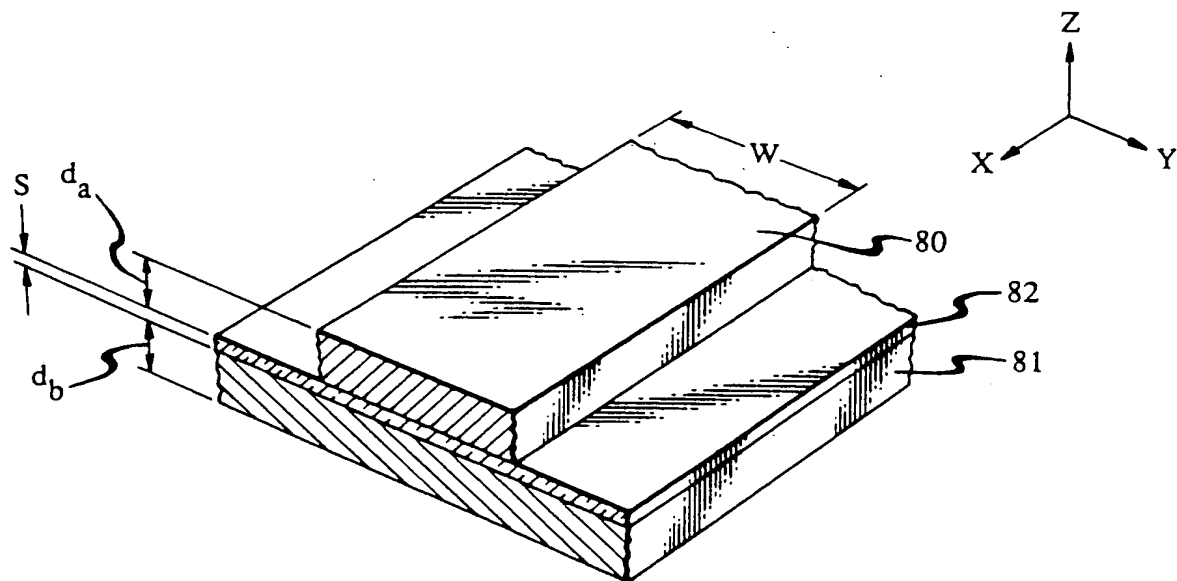
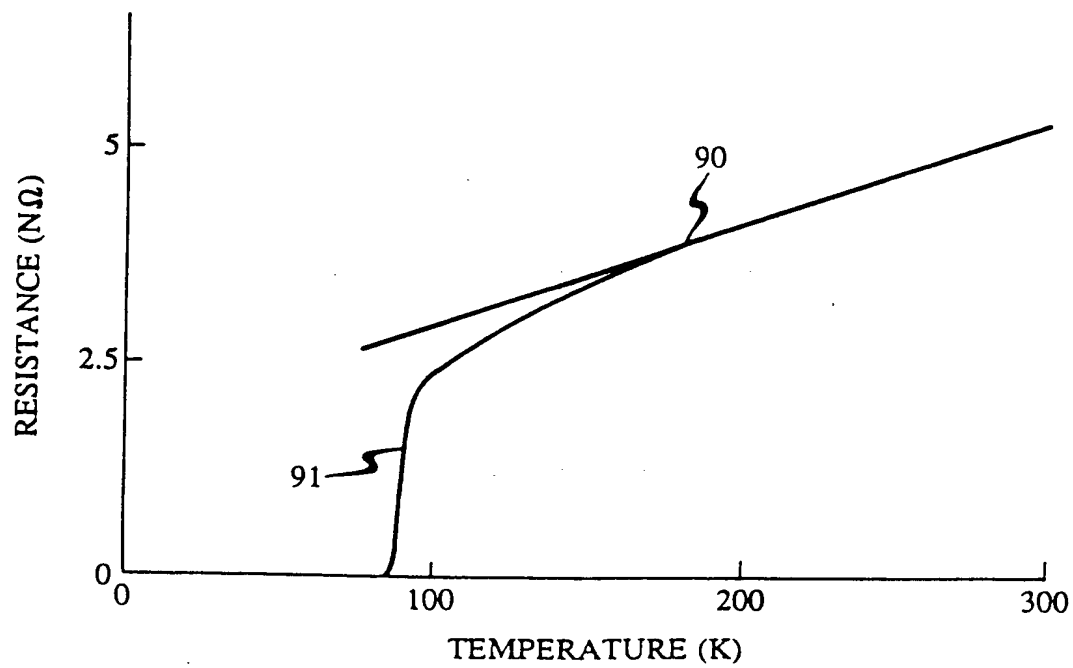


FIG. 11





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, P X	PHYSICAL REVIEW LETTERS, vol. 58, no. 9, 2nd March 1987, pages 908-910, The American Physical Society, New York, US; M.K.WU et al.: "Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure" * Page 908, paragraph 1 * ---	1-4, 6-10, 18, 20-23	H 01 L 39/14 H 01 L 39/12
P, X	PHYSICAL REVIEW LETTERS, vol. 58, no. 16, 20th April 1987, pages 1676-1679, The American Physical Society, New York, US; R.J.CAVA et al.: "Bulk superconductivity at 91 K in single-phase oxygen-deficient Perovskite Ba ₂ YCu ₃ O _{9-delta} " * Page 1679, column 1 *	1, 2, 6-10, 18, 20	
P, A	IDEM. ---	21-24	
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P, A	ELECTRONICS, vol. 60, no. 7, 2nd April 1987, pages 49-50, New York, US; T.NAEGELE: "Superconductivity drive gets hotter every day" * Page 49 *	22-23	H 01 L
E	EP-A-0 275 343 (IBM-BEDNORZ & MUELLER) * Column 4, lines 33-44 * --- -/-	1-4, 6-7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-12-1988	Examiner HAMMEL E.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



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Application Number

EP 88 30 0018

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-12-1988	Examiner HAMMEL E.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	